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Photoinduced anisotropy: new photopolarimetric setup for real-time measurements

L. Nikolova, T. Todorov, P. Sharlandjiev, and S. Stoyanov

We describe an experimental set up that measures material optical anisotropy and its eventual evolution in real time. The setup is based on a new photopolarimeter that measures the four Stokes parameters of quasi-monochromatic light quickly and simultaneously. The photoinduced anisotropy in the material optical constants is determined from the measured Stokes parameters. The features of the experimental setup are demonstrated by simultaneous measurement of the photoinduced changes in dichroism and birefringence of layers of rigid solutions of azodyes in polymethyl methacrylate, for which it is known that linearly polarized light orients the dye molecules.

Introduction

A significant number of photophysical and photochemical processes are accompanied by induced optical anisotropy. The measurement of that anisotropy and its evolution in time provides valuable information on the character of ongoing photoreactions and the structure of photoproducts. Optical anisotropy manifests itself as a function of wavelength for dichroism (different optical densities for light polarized parallel and perpendicular to the induced optical axis: $\Delta D = D_{\parallel} - D_{\perp} \neq 0$), birefringence (different refractive indices for light polarized parallel and perpendicular to the induced optical axis: $\Delta n = n_{\parallel} - n_{\perp} \neq 0$), or both.

One way in which to study the photoinduced dichroism is to measure $D_{\parallel}(t)$ and $D_{\perp}(t)$ consecutively with corresponding polarized light. This requires repeating the measurement of the photoprocess twice with great precision. Another way is to make use of linearly polarized light, oriented at $+45^\circ$ to the induced optical axis and, after an analyzer is oriented at -45° , to measure the rotation of light polarization. But if in addition to dichroism birefringence also exists in the sample, the interpretation of the signal after analysis is not straightforward. The signal after analysis may increase not only because of the polarization angle of rotation but also because the input linear polarization may become elliptic because of photoinduced birefringence in the sample.

To distinguish between the dichroism and birefringence a complete analysis of the state of polarization of the outgoing light is necessary, i.e., we must determine its Stokes parameters S_j ($j = 0, 1, 2, 3$).

The classical measurement of S_j requires the use of analyzer and compensator and at least four separate measurements with different orientations of their optical axes. This is not possible during a photoprocess evolution.

Azzam^{1,2} was the first to propose methods for fast determination of all Stokes parameters of light. The physical basis of these methods is the dependence of the reflection and transmission coefficients of beam splitters on light polarization. The light beam whose state of polarization is to be determined is divided into four beams by three beam splitters. The intensities of these four beams are measured and the corresponding electrical signals are processed by a computer to obtain the four Stokes parameters of light.

We proposed³ another scheme of a photopolarimeter for rapid and simultaneous measurement of Stokes parameters of quasi-monochromatic light based on the use of a new type of polarization beam splitter: a polarization holographic diffraction grating.⁴

We describe an experimental setup for simultaneous measurement of photoinduced dichroism and birefringence and their evolution in real time, making use of this new photopolarimeter (Stokesmeter).

Optical Scheme of the New Stokesmeter

The basic element of our Stokesmeter is a specific type of polarization beam splitter. It is a transmission holographic diffraction grating recorded in photoanisotropic material by two coherent waves with

The authors are with the Central Laboratory for Optical Storage and Processing of Information, Bulgarian Academy of Sciences, P.O. Box 95, Sofia 1113, Bulgaria.

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orthogonal circular polarizations. When materials with linear photoanisotropy are recorded, the interference pattern of such waves creates optical axes with periodic spatial variation of their directions.⁵ This periodic anisotropic structure has specific optical properties as follows:

The light beam L_0 incident on the grating is split into four beams: one undiffractedly reflected (L_1), one directly transmitted (L_2), and only two diffracted beams L_3 and L_4 (in $+1$ and -1 orders of diffraction).

For normal incidence the polarization of L_2 is the same as that of L_0 . The polarizations of L_3 and L_4 are independent of the polarization of L_0 ; they are always orthogonal, left and right circularly polarized.

The sum of the intensities I_3 and I_4 of beams L_3 and L_4 is also independent of the polarization of L_0 , in addition to

$$I_3/I_4 = I_R/I_L, \quad (1)$$

where I_R and I_L are the intensities of the right and the left circular components of incident beam L_0 .

For nonzero incident angles the reflection is polarization dependent and the corresponding changes in the polarization of L_2 , L_3 , and L_4 must be taken into account.

The scheme of the photopolarimeter is shown in Fig. 1. The polarization grating PG splits beam L_0 into four beams: L_1 – L_4 . L_2 passes through a linear polarizer LP whose axis is oriented at 45° to the plane of diffraction. The intensities I_j ($j = 1, 2, 3, 4$) of the four beams are measured by four photodetectors (D_1 – D_4), and the corresponding electrical signals i_j are digitized and processed by a microcomputer (MC) to calculate the four Stokes parameters S_i ($i = 0, 1, 2, 3$).

The following relations between the electrical signals and the Stokes parameters are derived:

$$\begin{aligned} i_1 &= k_1(RS_0 + \Delta RS_1), \\ i_2 &= k_2(1 - \eta)(T/2)[(1 - R)S_0 - \Delta RS_1 \\ &\quad + [(1 - R)^2 - \Delta R^2]^{1/2}S_2], \\ i_3 &= k_3(\eta/2)[(1 - R)S_0 - \Delta RS_1 \\ &\quad - [(1 - R)^2 - \Delta R^2]^{1/2}S_3], \\ i_4 &= k_4(\eta/2)[(1 - R)S_0 - \Delta RS_1 \\ &\quad + [(1 - R)^2 - \Delta R^2]^{1/2}S_3], \end{aligned} \quad (2)$$

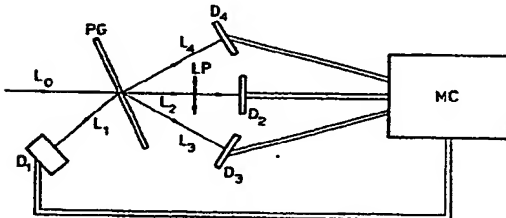


Fig. 1. Scheme of the photopolarimeter: PG, polarization diffraction grating; L_0 , analyzed light beam; L_1 , reflected beam; L_2 , undiffracted beam; L_3 , L_4 , diffracted beams; LP, linear polarizer; D_1 – D_4 , photodetectors; MC, microcomputer.

where k_j ($j = 1, 2, 3, 4$) is the proportionality constant for the conversion of the j th light beam into an electrical signal; $R = (R_s + R_p)/2$ and $\Delta R = (R_s - R_p)/2$, where R_s and R_p are the reflection coefficients for the s and p components of the L_0 beam; $\eta = (I_3 + I_4)/(1 - R)I_0$ is the diffraction efficiency of the grating measured with light linearly polarized at 45° to the incident plane; and $T = T_a T_g$, where T_g is the grating transmission and T_a is the maximum transmission of the linear polarizer.

From Eqs. (2) it is readily recognized that for the polarimeter calibration only six independent constants have to be determined:

$$\begin{aligned} P_1 &= 1/k_1, & P_2 &= 2/(1 - \eta)Tk_2, \\ P_3 &= 1/\eta k_3, & P_4 &= 1/\eta k_4, \\ P_5 &= R, & P_6 &= \Delta R. \end{aligned} \quad (3)$$

After the P_j constants are determined, the four Stokes parameters can be calculated by the following relations obtained from Eqs. (2) and (3):

$$\begin{aligned} S_0 &= P_1 i_1 + P_3 i_3 + P_4 i_4, \\ S_1 &= (1 - P_5)P_1 i_1/P_6 - P_5(P_3 i_3 + P_4 i_4)/P_6, \\ S_2 &= (P_2 i_2 - P_3 i_3 - P_4 i_4)/[(1 - P_5)^2 - P_6^2]^{1/2}, \\ S_3 &= (P_4 i_4 - P_3 i_3)/[(1 - P_5)^2 - P_6^2]^{1/2}. \end{aligned} \quad (4)$$

Because of the linear relations between i_j and S_i we can calibrate the device proposed by Azzam² and determine the apparatus matrix by measuring the values of i_j for four calibrating light beams with different states of polarization (with four independent Stokes vectors). Since at least two of the calibrating beams must have polarization that is substantially different from linear polarization, this operation is time-consuming and can be a source of significant errors. We used a different calibration technique based on the fact that the six constants, P_1 to P_6 , have a simple physical meaning and some of them can be determined independently with great precision. It was necessary to predetermine the mean reflection coefficient R of the beam splitter. Then the calibration of the polarimeter could be done by measuring the signals i_j for only two calibrating beams with linear polarizations (s and p) and by calculating the apparatus constants with

$$\begin{aligned} P_1 &= 2RS_0/(i_1^s + i_1^p), \\ P_2 &= 2(1 - R)S_0/(i_2^s + i_2^p), \\ P_3 &= 2(1 - R)S_0/(i_3^s + i_3^p), \\ P_4 &= 2(1 - R)S_0/(i_4^s + i_4^p), \\ P_5 &= R, \\ P_6 &= (i_1^s - i_1^p)R/(i_1^s + i_1^p), \end{aligned} \quad (5)$$

where S_0 is the intensity of light during the calibration procedure, and i_j^s and i_j^p are the signals from the

j th detector for the s - and p -polarized calibrating beams. The polarimeter was tested³ and it showed an experimental error of <0.01 when the normalized values of S_i were determined.

Setup for Real-Time Measurement of Photoinduced Anisotropy

The experimental setup for the investigation of photoinduced anisotropy is shown in Fig. 2. The photoprocess in sample H is induced by a light beam 1, which state of polarization is controlled by a linear polarizer P_1 . Probing light beam 2 must not contribute to the investigated photoprocess, so its intensity is chosen to be much lower (10^{-4}) than that of beam 1. Through polarizer P_2 beam 2 is linearly polarized at 45° to the polarization of beam 1. After the photoprocess is induced in sample H, probing beam 2 is analyzed by the photopolarimeter PP, and its Stokes parameters are determined.

The output Stokes vector S^{out} depends on the input Stokes vector and the optical properties of sample H, which are described by the corresponding Mueller matrix \mathcal{M} :

$$S^{\text{out}} = \mathcal{M} \cdot S^{\text{in}}. \quad (6)$$

In the coordinate system that is related to the photoinduced optical axis, the Mueller matrix is

$$\mathcal{M} = \begin{pmatrix} \frac{1}{2}(t_{\parallel}^2 + t_{\perp}^2) & \frac{1}{2}(t_{\parallel}^2 - t_{\perp}^2) & 0 & 0 \\ \frac{1}{2}(t_{\parallel}^2 - t_{\perp}^2) & \frac{1}{2}(t_{\parallel}^2 + t_{\perp}^2) & 0 & 0 \\ 0 & 0 & t_{\parallel}t_{\perp} \cos \delta & -t_{\parallel}t_{\perp} \sin \delta \\ 0 & 0 & t_{\parallel}t_{\perp} \sin \delta & t_{\parallel}t_{\perp} \cos \delta \end{pmatrix}, \quad (7)$$

where t_{\parallel} and t_{\perp} are the absolute values of the amplitude transmission for the polarization of light parallel and perpendicular to the optical axis, and δ is the phase shift between them induced by the sample.

In the same coordinate system the input Stokes vector is

$$S^{\text{in}} = I \cdot \begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad (8)$$

where I is the intensity of the probing light.

From Eqs. (6)–(8) it follows that the measured Stokes parameters are related to the optical transmission of the sample through

$$\begin{aligned} S_0 &= \frac{1}{2}I(t_{\parallel}^2 + t_{\perp}^2), \\ S_1 &= \frac{1}{2}I(t_{\parallel}^2 - t_{\perp}^2), \\ S_2 &= It_{\parallel}t_{\perp} \cos \delta, \\ S_3 &= It_{\parallel}t_{\perp} \sin \delta. \end{aligned} \quad (9)$$

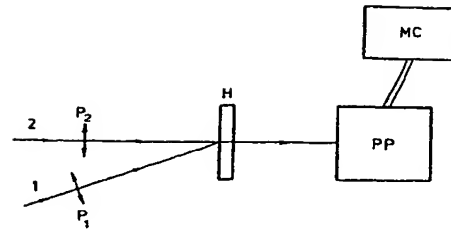


Fig. 2. Principal scheme of the experimental setup for polarimetric measurements: 1, laser beam that induces the photoprocess; 2, probing light beam; H, sample; P_1 , P_2 , linear polarizers; PP, photopolarimeter; MC, microcomputer.

Thus the optical constants of the sample and the photoinduced anisotropy can be determined by S_j :

$$\begin{aligned} D_{\parallel} &= \log_{10} \frac{I}{S_0 + S_1}, \\ D_{\perp} &= \log_{10} \frac{I}{S_0 - S_1}, \\ \Delta D &= D_{\perp} - D_{\parallel} = \log_{10} \frac{S_0 - S_1}{S_0 + S_1}, \\ \Delta n &= \frac{\lambda}{2d} \arctan \frac{S_3}{S_2}, \end{aligned} \quad (10)$$

where λ is the wavelength of light of the probe light, d is the sample thickness, and D is the optical density.

Results and Discussion

The new setup described above was tested by measuring the anisotropy of photoinduced changes in layers of rigid solutions of azodyes in a polymer matrix. The photoprocesses of these systems have been studied in Refs. 6 and 7. It is known that, after illumination with linearly polarized light, a reorientation and arrangement of the dye molecules occur, leading to optical anisotropy. Dichroism appears, and because of dispersion relations in addition to absorption, maximum birefringence shows up. We have studied the dichroism and birefringence in 100- μm -thick

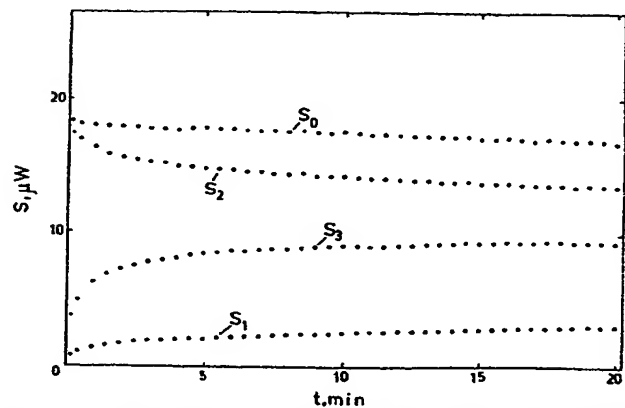


Fig. 3. Changes that occur in the Stokes parameters during the photoprocess.

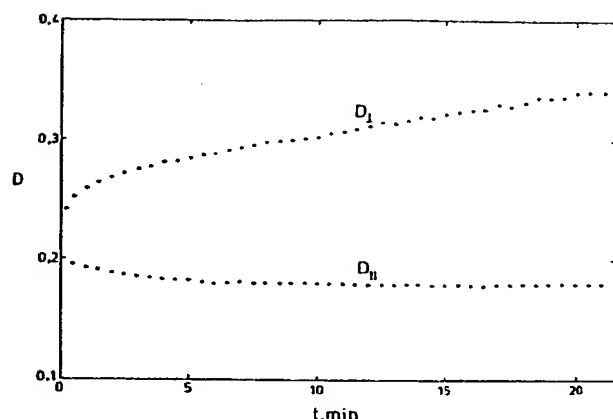


Fig. 4. Evolution of the dichroism and the birefringence.

layers of a rigid solution of azodye Sudan IV in polymethyl methacrylate.⁷ The dye absorption band is relatively large and has a maximum at ~ 500 nm. The photoprocess is induced with Ar^+ laser light at 488 nm. The probing light is from a He-Ne laser that has a wavelength at the edge of the dye absorption band. The Stokes parameters of the light that was transmitted through the He-Ne sample were measured at 10-s intervals after the beginning of the photoprocess.

The kinetics of the S_j parameters during the photoprocess are shown in Fig. 3. It can be seen that all four components of the Stokes vector are changing. This means that there is a simultaneous change in the sample mean absorption and in its anisotropy. From the values of S_j that were measured by using Eqs. (5), we determined $D_{||}$, D_{\perp} , ΔD , and Δn . The changes that took place during the photoprocess are shown in Figs. 4 and 5.

After Ar^+ laser illumination both dichroism and

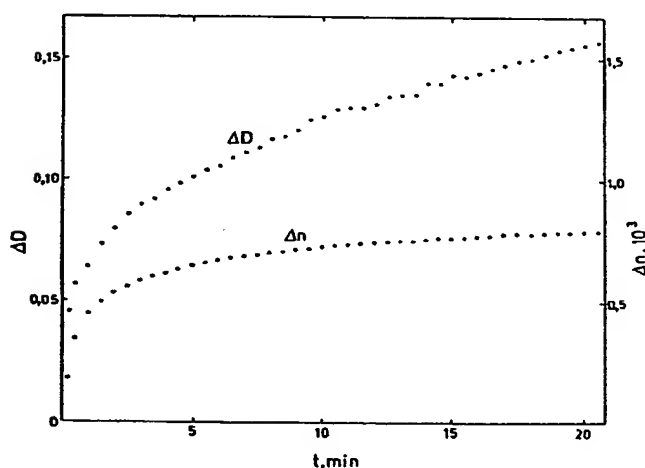


Fig. 5. Optical density change for the probing light with $\lambda = 633$ nm and polarization parallel ($D_{||}$) and perpendicular (D_{\perp}) to the polarization of light.

birefringence are induced in the sample. At the same time the mean optical density is increased, i.e., a new absorption band is created. At $\lambda = 633$ nm that band is more pronounced than the intrinsic absorption band. As can be seen the change in Δn does not match proportionally the evolution of ΔD , which means that the induced anisotropy is not due only to changes in the intrinsic absorption band. This result, unobserved until now, is obtained from the simultaneous measurement of dichroism and birefringence during the photoprocess. Apparently the difference in the evolution of Δn and ΔD can be explained by the contribution in Δn of a new absorption band. It is possible that it is the same absorption band whose formation is observed in Fig. 5.

A detailed understanding of the photoprocess in the azodye requires further investigation. We can state that the experimental setup described above would be of considerable help.

Conclusion

The polarimetric setup described above is an example of the potential of our photopolarimeter for real-time measurements. Because of the simultaneous measurement of all Stokes parameters the evolution of optical anisotropy, i.e., $D_{||}(t)$, $D_{\perp}(t)$, $\Delta D(t)$, and $\Delta n(t)$, can be studied. It is worth pointing out that the sign of Δn is also determined. These functions are informative in the studies of photophysical and photochemical reactions. As is well known, optical anisotropy can also be induced by other means: electrical, mechanical, etc. The experimental setup and the deduced relations for the induced dichroism and birefringence can be applied only if the direction of the induced optical axis is known in advance.

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